

Supporting Information

Asymmetric Thiophene/Pyridine Flanked Diketopyrrolopyrrole Polymers towards High Performance Polymer Ambipolar Field-effect Transistors and Solar Cells

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1. Measurement and characterization

Reaction solvents were distilled from Na and benzophenone under nitrogen immediately prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer using CDCl_3 as the solvent and chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane standard. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 under an N_2 flow at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

2. Synthetic Procedures and Characterizations

Compound 1. To a dried three necked flask were added NaH (4.4 g, 60% w/w, 112 mmol), dimethyl carbonate (7.2 g, 40.0 mmol) and toluene (40 mL) under nitrogen. After the mixture was heated to reflux, a solution of 2-acetylthiophene (4.3 mL, 40.0 mmol) in toluene (20 mL) was added dropwise. After the evolution of hydrogen ceased, the reaction was cooled down to room temperature. Glacial acetic acid (12 mL) was added dropwise and then ice-cold water was slowly added. The mixture was dilute with 200 mL of ethyl acetate. The organic layer was separated, washed with water (40 mL) and brine (40 mL) and dried over Na_2SO_4 , concentrated in vacuum. The residue was purified by column chromatography over silica gel using a mixture of petroleum ether and EtOAc as eluent and the desired methyl 3-oxo-3-(thiophen-2-yl)propanoate was obtained in 93% yields.

Compound 2. Methyl 3-oxo-3-(thiophen-2-yl) propanoate (6.1g, 33.0 mol), methyl 2-bromoacetate (5.0 g, 33.0 mol), sodium carbonate (6.9 g, 50.0 mol), acetone (40 mL) and 1,2 dimethoxyethane (10 mL) were added to a flask. After refluxing for 16 h, the reaction mixture was poured into water and extracted with EtOAc. The organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuum. The residue was purified by column chromatography over silica gel using a mixture of petroleum ether and EtOAc as eluent and the desired dimethyl 2-(thiophene-2-carbonyl)succinate was obtained in 98% yields.

Compound 3. Acetic acid (50 mL) and ammonium acetate (28.0 g, 0.36 mol) were added to dimethyl 2-(thiophene-2-carbonyl)succinate, the mixture stirred under reflux for 6 h. The product was obtained by filtration after cooling to $0\text{ }^\circ\text{C}$ and then washed with boiling water followed with boiling methanol. The desired methyl 5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate was obtained in 46% yields. ^1H NMR (400 MHz, CDCl_3): δ 8.51, (br s, 1H), 7.79 (d, $J = 3.6\text{ Hz}$, 1H), 7.59 (d, $J = 4.9\text{ Hz}$, 1H), 7.17 (dd, $J = 4.2, 4.7\text{ Hz}$, 1H), 3.78 (s, 3H), 3.54 (s, 2H); MS (EI) calcd. for $\text{C}_{10}\text{H}_9\text{NO}_3\text{S}^+$ ($[\text{M}]^+$): 223, found 223.

Compound 4. Sodium (0.68 g, 29.6 mmol) was added to a stirred solution of iron chloride (3 mg) in 2-methylbutan-2-ol (30 mL) and heated to reflux until the complete consumption of sodium. The solution was cooled to $80\text{ }^\circ\text{C}$ and 5-bromopicolinonitrile (1.83 g, 10.0 mmol) was added in small portions and 5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1.88 g, 8.4 mmol) was added in one portion. The resulting mixture was stirred at $120\text{ }^\circ\text{C}$ for 2 h. The reaction was quenched by the addition of glacial acetic acid (5 mL) in methanol (20 mL) and the mixture stirred at $90\text{ }^\circ\text{C}$ for 10 min. The precipitate was collected by filtration and washed with water and methanol and

dried in vacuum. The 3-(5-bromopyridin-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione was obtained in 77% yield and used without further purification.

Compound 5. To a solution of 3-(5-bromopyridin-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-(2*H*,5*H*)-dione (2.24 g, 6.0 mmol) and 18-crown-6 (10 mg) in DMF (50 ml) was added K₂CO₃ (3.3 g, 24.0 mmol) and heated to 120 °C for 1 h, then 11-(bromomethyl)tricosane (10.03 g, 24.0 mmol) was added dropwise. After being stirred at 120 °C overnight, the reaction mixture was poured into water and extracted with chloroform. The combined organic layers were washed with water, dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography over silica gel using a mixture of petroleum ether and dichloromethane as eluent. Finally, the result product was recrystallized from ethanol. 39% yield; deep red solid; TLC (PE: DCM, 3:1 v/v): R_f = 0.20; ¹H NMR (300 MHz, CDCl₃): δ 9.06 (dd, *J* = 0.9, 3.9 Hz, 1H), 8.84 (d, *J* = 8.6 Hz, 1H), 8.72 (d, *J* = 2.3 Hz, 1H), 7.98 (dd, *J* = 2.4, 8.6 Hz, 1H), 7.68 (dd, *J* = 0.9, 5.0 Hz, 1H), 7.29 (dd, *J* = 4.1, 4.8 Hz, 1H), 4.31 (d, *J* = 7.3 Hz, 2H), 4.00 (d, *J* = 7.7 Hz, 2H), 1.90, (br s, 1H), 1.63, (br s, 1H), 1.21-1.08 (m, 80H), 0.89-0.85 (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 162.41, 161.87, 149.96, 146.48, 142.87, 142.34, 139.53, 136.65, 131.62, 129.48, 128.65, 127.99, 121.85, 110.74, 108.65, 46.33, 46.22, 38.25, 37.76, 31.94, 31.48, 31.19, 30.04, 29.70, 29.65, 29.56, 29.38, 26.41, 26.21, 22.70, 14.13; HRMS (MALDI-TOF-MS) calcd. for C₆₃H₁₀₅BrN₃O₂S⁺ ([M+H]⁺): 1046.7105, found 1046.7106.

Compound 6. 3-(5-Bromopyridin-2-yl)-2,5-bis(2-decyltetradecyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4(2*H*,5*H*)-dione (1.047 g, 1.0 mmol) was dissolved in 15 mL chloroform. The solution was purged with argon for 5 min and then *N*-bromosuccinimide (0.196 g, 1.1 mmol) was added in small portions. After stirring at room temperature overnight, the mixture was poured into 100 mL methanol and filtered. The residue was subsequently recrystallized from ethanol. 73% yield; purple solid; TLC (PE: DCM, 3:1 v/v): R_f = 0.25; ¹H NMR (300 MHz, CDCl₃): δ 8.83 (d, *J* = 8.6 Hz, 1H), 8.82 (d, *J* = 8.6 Hz, 1H), 8.72 (d, *J* = 2.0 Hz, 1H), 7.98 (dd, *J* = 2.4, 8.6 Hz, 1H), 7.25 (d, *J* = 4.3 Hz, 1H), 4.30 (d, *J* = 7.4 Hz, 2H), 3.92 (d, *J* = 7.7 Hz, 2H), 1.88, (br s, 2H), 1.62, (br s, 2H), 1.21-1.10 (m, 80H), 0.90-0.85 (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 162.15, 161.78, 150.03, 146.37, 142.79, 141.43, 139.58, 136.53, 131.64, 130.87, 128.04, 122.02, 120.02, 110.61, 108.83, 46.40, 46.31, 38.25, 37.80, 31.94, 31.47, 31.19, 30.03, 29.99, 29.70, 29.65, 29.57, 29.38, 26.39, 26.19, 22.71, 14.13; HRMS (MALDI-TOF-MS) calcd. for C₆₃H₁₀₄Br₂N₃O₂S⁺ ([M+H]⁺): 1124.6211, found 1124.6211.

3. Thermal and electrical property

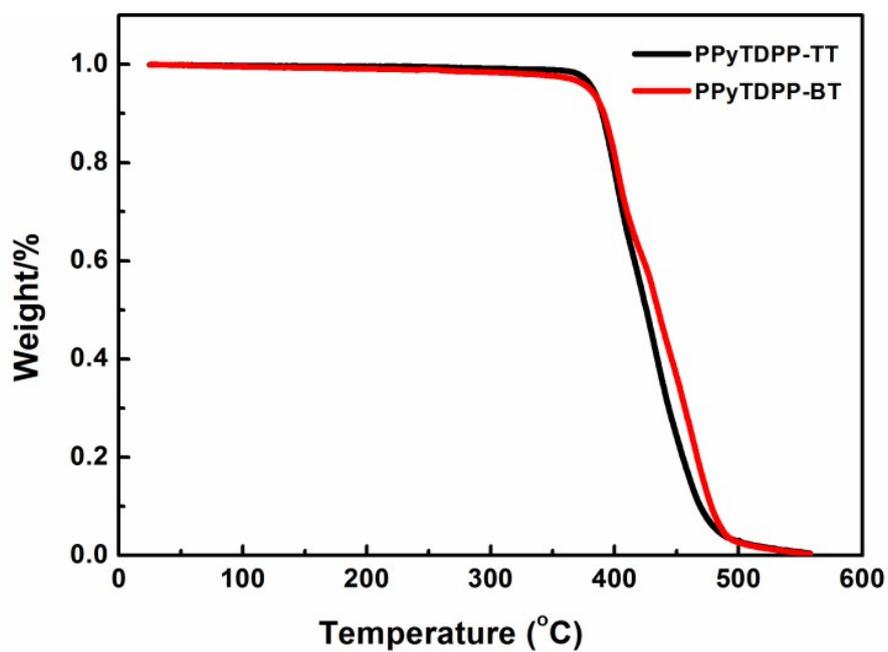


Fig. S1 TGA of PPyTDPP-TT and PPyTDPP-BT.

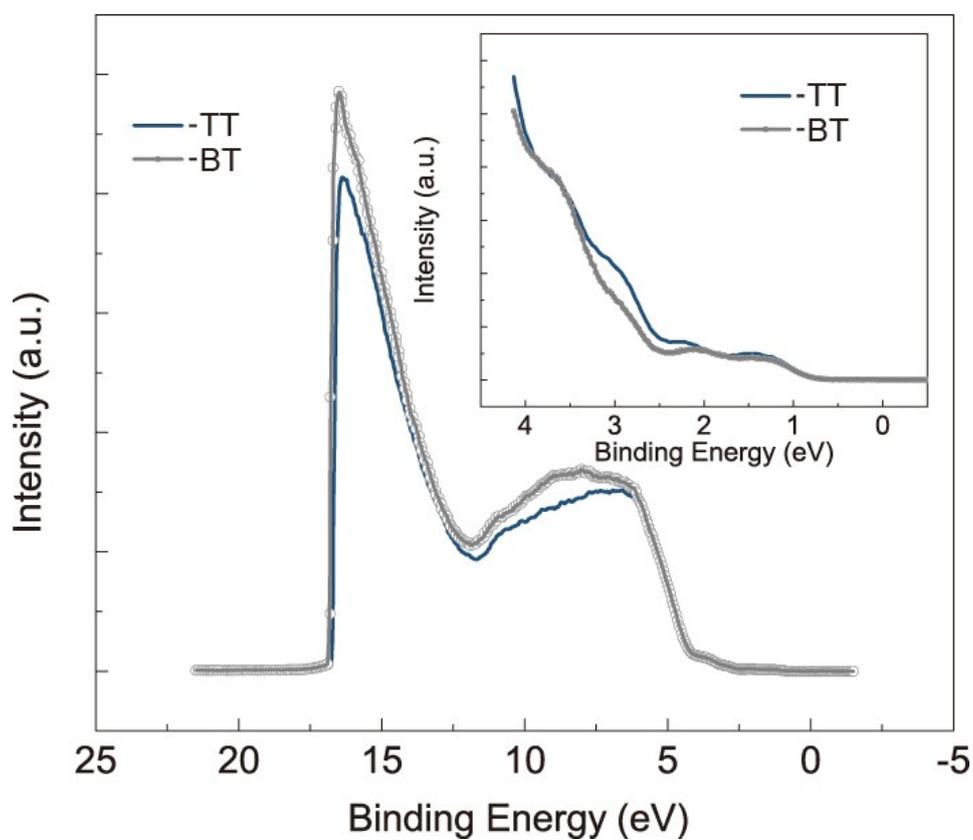
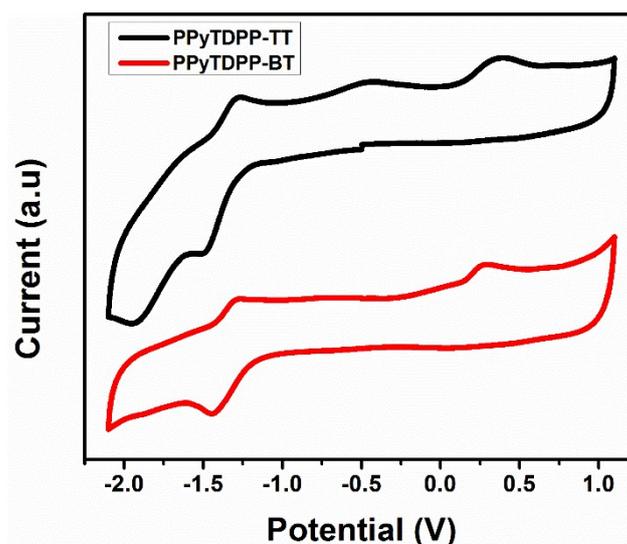


Fig. S2 UPS of PPyTDPP-TT and PPyTDPP-BT. HOMO = $h\nu + E_{\text{cutoff}} - E_F$, $h\nu = 21.22$ eV.



- **Fig. S3** CV curves of **PPyDPP-TT** and **PPyDPP-BT** in *o*-dichlorobenzene. (Scan rate = 100 mV s⁻¹, electrolyte, 0.1 M n-Bu₄NPF₆) with acetylferrocene as reference.

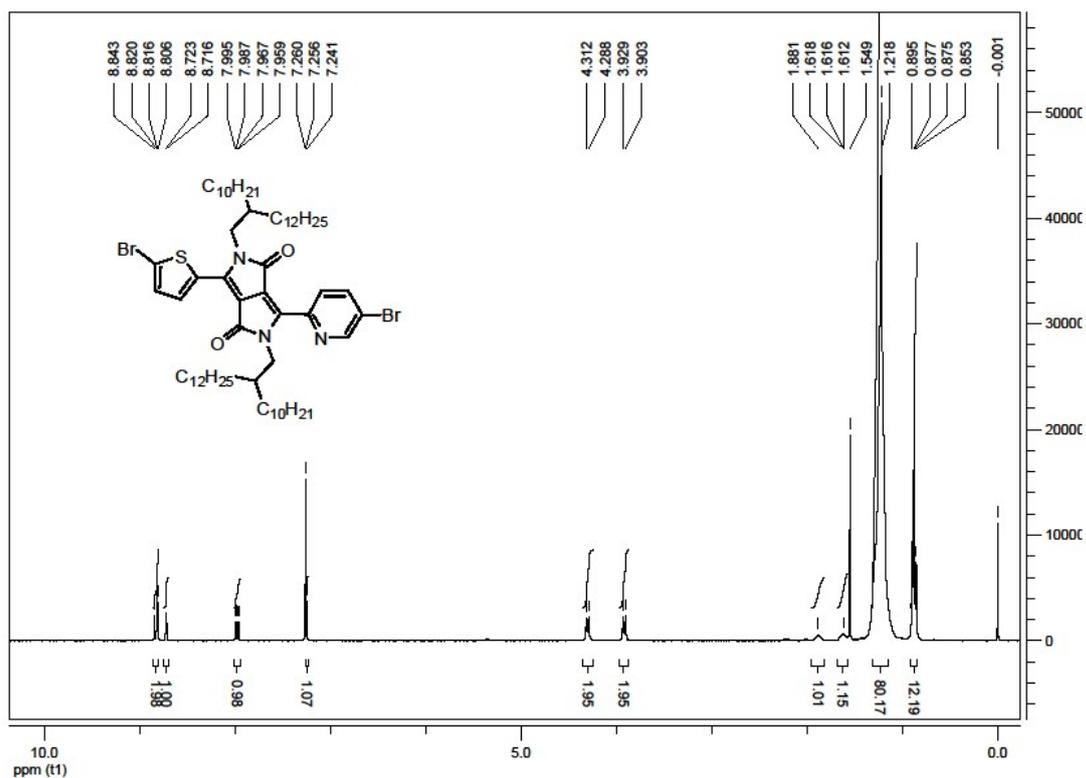
Table S1 Optimized photovoltaic performances with **PPyDPP-TT** and **PPyDPP-BT** after blending with PC₇₁BM in different ratios under DIO volume of 5%.

Polymer	Ratio [w/w]	Voc [V]	Jsc [mA/m ²]	FF [%]	PCE [%]
PPyDPP-TT	1:1.5	0.824	8.79	57.48	4.16
	1:1	0.838	8.14	58.42	3.99
PPyDPP-BT	1:1.5	0.774	11.51	68.61	6.11
	1:1	0.790	9.71	66.83	5.13

Table S2 Optimized photovoltaic performances with **PPyDPP-TT** and **PPyDPP-BT** (as acceptor) after blending with P3HT (1:2, w/w).

Polymer	Voc [V]	Jsc [mA/m ²]	FF [%]	PCE [%]
PPyDPP-TT	0.815	1.83	55.23	0.82
PPyDPP-BT	0.901	1.33	49.29	0.59

¹H NMR PyTDPP



¹³C NMR PyTDPP

